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Mini review

Nanostructured materials for water splitting - state of the art and future needs: A mini-review

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ABSTRACT

Sustainable hydrogen production is the essential prerequisite for an envisioned hydrogen economy. The solar mediated water splitting process, which employs semiconductors that serve as light absorbers and photocatalysts, is a promising approach for the generation of hydrogen. Electrocatalysts have also been widely used as co-catalysts to increase the kinetics of water splitting. This mini-review surveys state-of-the-art electrocatalysts and photocatalysts with nanostructured features, and discusses future requirements in the area of solar-driven water splitting.

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Contents

1. Introduction

Fossil fuels, which currently provide 86% of the energy to drive global anthropogenic demand, are anticipated to have the capacity to endure for ~50 more years, if we maintain our present rate of consumption [1]. More importantly, the combustion of fossil fuels generates enormous volumes of CO_2, which contributes significantly to climate change. To effectively reduce CO_2 emissions, it is critical to develop clean and renewable energy sources to incrementally replace fossil fuels. Among the various alternative energy strategies, the construction of an energy infrastructure that utilizes hydrogen as the primary carrier may hold great promise for a clean and sustainable energy future.

In achieving this, the effective production and storage of hydrogen are key elements. Steam methane reforming, coal gasification, and water splitting are the three primary approaches for the production of hydrogen. Among them, solar, or other renewable resource driven water splitting comprises the most sustainable strategy [2]. Solar mediated water splitting engages one of the most fascinating processes, which involves capturing ambient sunlight and converting its electromagnetic energy directly into chemical energy in the form of molecular bonds within hydrogen gas (H_2), a clean and recyclable energy carrier [3]. The attractiveness and advantages of solar water splitting include abundant water resources, small reaction potential difference (1.23 eV), and zero CO_2 generation [1].

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Photocatalytic, photoelectrochemical (PEC), and photovoltaic–electrolysis systems are feasible approaches for water splitting in the production of hydrogen via sunlight. Photocatalysts with maximum solar light absorption, superior charge transport, and long-term stability are desirable. On the other hand, electrocatalysts have been widely employed as co-catalysts to enhance efficiencies. Noble metal based catalysts such as platinum, palladium, ruthenium oxide, and iridium oxide exhibit high catalytic functionality for water splitting [1,4]. However, for practicable commercial applications, electrocatalysts comprised of elementally abundant and less expensive materials are far more attractive. Recently, increasing attention has been paid to the development of earth-abundant nanomaterials as electrocatalysts and photocatalysts for water splitting [5]. In this mini-review, we survey state-of-the-art electrocatalysts and photocatalysts that are under development for solar-driven water splitting, discuss strategies for augmenting the efficacy and performance of these catalysts, and highlight future requirements in this field.

2. State-of-the-art electrocatalysts for water splitting

Generally, the utilization of electrocatalysts is a common strategy for improving the performance of water splitting. Catalytic activity is the most important parameter in the evaluation of their performance, which may be expressed by Tafel plots for the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). To obtain an equivalent current, a lower overpotential for driving each reaction is more desirable. Long-term stability is another key parameter in assessing the quality of electrocatalysts for water splitting. There is a great interest in the development of naturally abundant nanomaterials that possess high activity for their respective reactions and high stability for practical applications [6,7]. Numerous studies on nanostructured electrocatalysts for water splitting have been published; however, no standard protocols for comparing the performance of electrocatalysts for solar water splitting have yet been established.

Recently, McCrory and co-workers suggested a benchmarking protocol for the rapid and preliminary evaluation of catalyst performance, where 18 electrocatalysts for HER and 26 electrocatalysts for OER were tested under conditions that were relevant to an integrated solar water-splitting device in aqueous acidic or alkaline solutions [8]. Fig. 1 presents the overpotential of each catalyst that is required to achieve a magnitude current density of 10 mA cm^{-2} with respect to its geometric area, which was selected due to the desired solar-to-hydrogen conversion efficiency of 10% under one sun illumination.

As seen in Fig. 1, RuO_2 and IrO_2 are ranked as the top catalysts for water oxidation in both acidic and basic media; while Pt is considered as the benchmarking electrocatalyst for HER. However, the high cost of precious metals hinders their practical application. Subsequently, research interests have shifted to the investigation of naturally abundant metal resources, such as Ni, Fe, and Co based materials. Gao et al. reported that nanostructured α-$Ni(OH)_2$ spheres exhibited a small overpotential of 0.331 V at 10 mA cm^{-2}, and a small Tafel slope of ~42 mV dec^{-1}, which were comparable to RuO_2 catalysts [9]. In addition, the α-$Ni(OH)_2$ spheres exhibited improved durability over RuO_2. A study conducted by Ma et al. showed that a Co_3O_4/C porous nanowire array had the capacity to achieve a current density of 10 mA cm^{-2} at an overpotential of 0.29 V, which was lower than that of IrO_2/C (0.31 V), and other reported noble-metal catalysts [10]. Kim and Choi investigated a FeOOH/NiOOH dual layer as an oxygen evolution catalyst, which significantly improved the catalytic activity of $BiVO_4$ photoelectrode for solar water splitting [11].

As shown in Fig. 1, Pt is considered as the benchmarking electrocatalyst for HER due to its small overpotential and high kinetics. However, its limited supply and high cost make its application in commercial solar water splitting processes unfeasible. A number of non-noble metal materials, such as transition-metal chalcogenides, carbides, and complexes, as well as metal alloys, have recently been widely prepared and evaluated for use as catalysts, or catalyst supports for HER. For instance, electrodeposited NiMo and NiMoCo nanomaterials, which possess a one-hundred-fold larger electrochemically active surface area (ECSA) than Pt, demonstrated a similar geometric activity in acidic media to that of Pt, achieving 10 mA cm^{-2} at −0.045 V and −0.05 V, respectively, with no loss of activity following 2 h of constant polarization [8]. In addition, Karunadasa et al. synthesized a well-defined Mo^{IV}–disulfide complex, which showed promise as a low-cost alternative to platinum for the electrocatalytic generation of hydrogen [12]. An additional study carried out by Sun and co-workers demonstrated that carbon nanotubes decorated with cobalt phosphide (CoP) nanocrystals exhibited superior HER catalytic activity in acidic media [13]. Furthermore, it is worthy to mention that graphene and reduced graphene oxide have gained extensive attention for water splitting as an electron mediator or a co-catalyst, which may trap the excited electrons and suppress the recombination of charge carriers.

3. State-of-the-art photoanodes and photocathodes for water splitting

Nanostructured photoactive materials are essential for efficient solar water splitting, and the requirements for an ideal semiconductor include: (i) proper positions of the conduction and valence bands to straddle the HER and OER potentials; (ii) relatively small band gap for visible light absorption; (iii) high stability under sunlight irradiation in acidic/basic aqueous solutions; (iv) efficient charge transport; and (v) low overpotentials for the oxidation/reduction of water [14]. However, no single semiconductor has yet been identified that meets all of the above criteria. Various materials and synthesis techniques have been explored toward enhancing the performance of the solar water splitting

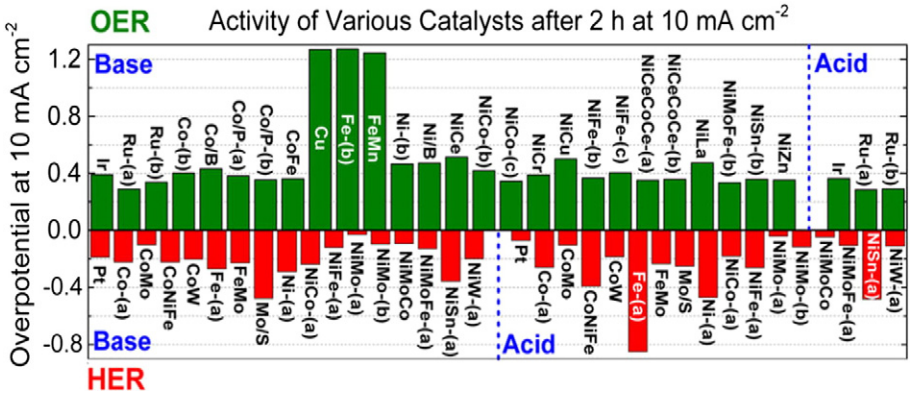

Fig. 1. List of overpotentials required for different electrocatalysts in hydrogen or oxygen evolution to achieve a current density magnitude of 10 mA cm^{-2} per geometric area current density, in basic and acidic solutions, respectively, under 1 sun illumination. Adapted with permission from Ref. [8] Copyright© 2015 American Chemical Society.

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